# Courant Institute of Mathematical Sciences

## AEC Computing and Applied Mathematics Center

# Short Range Anti-Correlation of Electrons in the Hydrogen Molecule

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# SHORT RANGE ANTI-CORRELATION OF ELECTRONS

## IN THE HYDROGEN MOLECULE

by

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ABSTRACT

The coulomb repulsion between the electrons is represented as the sum of a long-range unperturbed part and a short-range perturbation. Wang's form of the Heitler-London approximation is used as the approximate eigenfunction for the unperturbed hamiltonian. The correction for the short-range perturbation is made by a method based on the impulse approximation.

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# INTRODUCTION

At points where two or more electrons coincide, the analytic behavior of trial functions commonly used in Rayleigh-Ritz calculations differ from that of solutions of Schrodinger's equation. Consequently, these trial functions are poor approximations to the correct eigenfunctions in domains where the distance between two electrons is sufficiently small. We attempt to study the resulting error in the Rayleigh-Ritz energy estimate by improving the trial function in these domains. We do not expect to achieve this by superposing functions with the incorrect analytic behavior, for this leads to slow convergence.[1],[2] Instead, we try to satisfy the singularity condition, at least formally. We separate the coulomb repulsion into two parts, a long-range unperturbed part and a short-range perturbation. This separation is arbitrary and contains parameters which are adjusted at a later stage of the calculation. We assume the ground state eigenfunction of the unperturbed hamiltonian is approximated well by a known function, such as the Heitler-London, molecular orbital, or small superpositions of these. We account of the perturbation by an adaptation of the impulse approximation,[3]-[6] which applies to short-range forces which need not be weak. The parameters used in decomposing the coulomb repulsion are finally adjusted by a self-consistency condition. The formal details are described in Section 1.

The integrals needed for a direct variational calculation are difficult to evaluate. To circumvent this problem, we use a simple non-variational condition which makes the ground state energy of the perturbed and unperturbed hamiltonians approximately equal, assuming the basic model is valid. If this condition can be applied to adjusting the parameters in the unperturbed hamiltonian, the effect of the perturbation would be small and the difficult integrals could be estimated crudely, since they do not occur in the zero-order problem. The condition involves an integral which is much simpler than those needed for the variational estimate, but the evaluation still requires further approximation. Here we use an approximation which simplifies the calculation enormously, and also has an attractive physical interpretation. However, it seems that this approximation is too drastic. Additional study of the relevant integral seems practical as well as useful. The details are described in Section 11.

To have a definite problem, we calculate the ground state energy of the hydrogen molecule. We expect the unperturbed problem to be relatively simple, while the effects of the short-range perturbation probably do not depend on the details of the molecule, but only on the general features of the un-perturbed eigenfunction. Wang's modification of the Heitler-London trial function[7] is assumed adequate for the un-perturbed problem. We note that the extension to problems

involving more than two electrons is straightforward, similar
to the generalization of the impulse approximation.[6] This
is the motivation for this study since it is known that
electronic energies of the hydrogen molecule may be calculated
with high accuracy if the distance between electrons is used
directly in the trial function.[8],[9]

# I.  GENERAL THEORY

If the protons are infinitely heavy, the hamiltonian for the hydrogen molecule is

$$(1.1) \qquad H = K + V_A + \frac{1}{r}$$

Here  $K$  is the kinetic energy,  $V_A$  the attraction between electrons and protons,  $r$  the distance between electrons, and atomic units are used.  The unperturbed hamiltonian is obtained by replacing  $(1/r)$  by a modified repulsion  $V_{eo}(r)$

$$(1.2) \qquad H_o = K + V_A + V_{eo}(r)$$

$$(1.3) \qquad V_{eo}(r) = \frac{1 - e^{-\lambda r}}{r} + \mu \, e^{-\lambda r}$$

The parameters  $\lambda$  and  $\mu$  are determined later.  The functional form (1.3) is used for convenience, and eliminates the divergence in the energy but not in all its gradients.  This could clearly be done by using a different form of  $V_{eo}$ , namely an integral function of  $r^2$  rather than  $r$ .  Clearly the term in (1.3) proportional to  $\mu$  compensates the repulsion removed at small  $r$ .  For each  $\lambda$ , we expect some positive  $\mu$  will make the ground state eigenvalues of  $H_o$  and  $H$  equal. We now use Wang's form for the spatial part of the unperturbed trial function

$$(1.4) \qquad \phi = \frac{1}{4\pi} \frac{1 + P_{12}}{2} \exp\left[-\kappa(r_1 + |\, \underset{\sim}{r}_2 - \underset{\sim}{b}\,|)\right]$$

Here $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ are position vectors of the electrons, $b$ is the distance between protons, and $P_{12}$ exchanges $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$. We want a function which approximates the ground state eigenfunction of $H$ almost as well as $\phi$ approximates the corresponding eigenfunction of $H_o$.

We introduce notation

$$(1.5) \qquad \underset{\sim}{R} = \frac{1}{2}(\underset{\sim}{r}_1 + \underset{\sim}{r}_2)$$

$$(1.6) \qquad \underset{\sim}{r} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$$

$$(1.7) \qquad V_{el}(r) = \frac{1}{r} - V_{eo}(r) = e^{-\lambda r}(\frac{1}{r} - \mu)$$

We define a basic set of functions of $\underset{\sim}{r}$

$$(1.8) \qquad \left[-\nabla^2 + V_{el}(r)\right] f(k\ell;r) Y_{\ell m}(\theta\Phi) = k^2 f(k\ell;r) Y_{\ell m}(\theta\Phi)$$

Here $(r\theta\Phi)$ are spherical coordinates of $\underset{\sim}{r}$, $Y_{\ell m}(\theta\Phi)$ is a spherical harmonic, $\nabla^2$ is the Laplacian operator with respect to coordinates of $r$, and $f(k\ell;r)$ is a regular solution of (1.8). To define the normalization of $f$, we use the conventional condition that for values of $(kr)$ much greater than unity

$$(1.9) \qquad f(k\ell;r) \sim \frac{\sin[kr - \frac{1}{2}\ell\pi + \eta(k\ell)]}{kr}$$

Here $\eta(k\ell)$ is independent of $r$ and is the usual phase shift. The set $f(k\ell;r) Y_{\ell m}(\theta\Phi)$ is complete if the operator on the left of (1.8) has no bound state. This holds for all $\ell$ if it holds for $\ell = 0$, and a sufficient condition for the non-existence of a bound state is equivalent to a necessary condition for the existence of one.[10]

$$(1.10) \qquad \int_{r_0}^{\infty} r\left[-V_{el}(r)\right] dr < 1$$

Here $r_0$ is the point where $V_{el}(r)$ vanishes, namely $(1/\mu)$.

$$(1.11) \qquad \frac{\mu}{\lambda^2} \exp(-\lambda/\mu) < 1$$

Condition (1.11) is imposed upon all parameter sets $(\lambda,\mu)$. A unitary transformation $U$ is defined explicitly

$$(1.12) \qquad U j_{\ell}(kr) Y_{\ell m}(\theta\Phi) = f(k\ell;r) Y_{\ell m}(\theta\Phi)$$

An operator equation follows from (1.12)

- 8 -

$$(1.13) \qquad U^{-1}\left[-\nabla^2 + V_{el}(r)\right]U = -\nabla^2$$

The basic assumption of this paper is that $U\phi$ is the desired approximate eigenfunction of $H$. This is written out explicitly using Fourier expansions

$$(1.14) \qquad \phi = \frac{2}{\pi} \sum_{\ell m} Y_{\ell m}(\theta\underline{\Phi}) \int_0^\infty A(k\ell m;\underline{R}) j_\ell(kr) k^2 \, dk$$

$$(1.15) \qquad U\phi = \frac{2}{\pi} \sum_{\ell m} Y_{\ell m}(\theta\underline{\Phi}) \int_0^\infty A(k\ell m;\underline{R}) f(k\ell;r) r k^2 \, dk$$

Here equation (1.14) simply defines the expansion coefficients $A(k\ell m;\underline{R})$ , and (1.15) is the explicit form of $U\phi$. The analogy to the original definition of the impulse approximation is clear.[11]

$$(1.16) \qquad E S = (\phi,H_0\phi) + \ulcorner$$

$$(1.17) \qquad S = (U\phi,U\phi) = (\phi,\phi)$$

$$(1.18) \qquad \ulcorner = (U\phi, (V_A + V_{eo}) U\phi) - (\phi, (V_A + V_{eo}) \phi)$$

In principle the requirement that $E$ is a minimum determines the parameters in $\phi$ and $V_{eo}(r)$ simultaneously.

Unfortunately the integrals denoted by $\Gamma$ are difficult to evaluate. The part involving $V_A$ is expected to be most important and its physical meaning is clear from the impulse approximation.[12] The commutator of U with $V_A$, which determines the relevant part of $\Gamma$, is determined by the variation of $V_A$ over domains in which $V_{el}(r)$ is significantly different from zero. If this variation is large, will be large and positive. This is true even if H and $H_o$ have exactly the same eigenvalues and if $\phi$ is also the exact eigenfunction of $H_o$. The point is that in this case $U\phi$ would be a poor approximation to the correct eigenfunction of H. For this reason, the method is not expected to be useful for the helium atom, where the maximum probability of finding two electrons close is near the origin, where $V_A$ varies rapidly. In the hydrogen molecule, the corresponding probability has its maximum at a saddle point of $V_A$. The part of $\Gamma$ which involves $V_{eo}$ is not directly involved in limiting the range of $V_{el}$, and is expected to be less important.

An approximation formally independent of the model, but physically related, is that the difference between $U\phi$ and $\phi$ involves only terms with $\ell = 0$ in (1.14) and (1.15). This implies the centrifugal barrier masks the short-range potential $V_{el}(r)$ for higher values of $\ell$. But the evaluation of $\Gamma$ remains difficult even with this approximation.

## II. NON-VARIATIONAL CONDITION ON THE PARAMETERS OF $V_{el}(r)$

If $\phi$ and $U\phi$ are good approximations to the ground state eigenfunctions of $H_O$ and $H$ respectively, the usual manipulation involving hermiticity leads to

$$(2.1) \qquad (\phi, V_{el} U\phi) = (E - E_O)(\phi, U\phi) = 0$$

Here $E_O$ and $E$, the ground state eigenvalues of $H_O$ and $H$ respectively, are approximately equal. If $\phi$ and $U\phi$ are expanded in spherical harmonics as in (1.14) and (1.15), only terms with $\ell = 0$ are assumed to be important. This is a consequence of the short-range character of $V_{el}(r)$, and is equivalent to the approximation mentioned in the last paragraph of Section 1. Direct substitution leads to

$$(2.2) \qquad (\tfrac{2}{\pi})^2 \int A(k';\underset{\sim}{R}) A(k;\underset{\sim}{R})(k'|V_{el}||k) k'^2 dk' k^2 dk \, d^3R = 0$$

$$(2.3) \qquad (k'|V_{el}||k) = \int_O^\infty j_O(k'r) V_{el}(r) f(k;r) r^2 \, dr$$

We use the notation of suppressing the indices $(\ell, m)$ when only $\ell = 0$ is involved. The integral on the right of (2.2) is simpler than the integrals $\Gamma$ defined by (1.18), but further simplifications are needed to evaluate it. One of the

simplest approximations is to expand $(k'|V_{el}||k)$ in powers of $(k^2 - k_o^2)$ and $(k'^2 - k_o^2)$, keeping only powers zero and one, where $k_o^2$ is some average value of $k^2$. This expansion is used in the theory of scattering by short-range potentials, such as the "effective range" theory.[13] Condition (2.2) becomes

$$(2.4) \qquad (k_o|V_{el}||k_o) = -\frac{\sin \eta(k_o)}{k_o} = 0$$

$$(2.5) \qquad k_o^2 = \frac{\left(\frac{2}{\pi}\right)^2 \int A(k';\underset{\sim}{R})A(k;\underset{\sim}{R}) \; k^2k'^2 dk'k^2 dk \; d^3R}{\left(\frac{2}{\pi}\right)^2 \int A(k';\underset{\sim}{R})A(k;\underset{\sim}{R}) \; k'^2 dk'k^2 dk \; d^3R}$$

$$(2.6) \qquad k_o^2 = \frac{\int \phi_o(\underset{\sim}{R})\left[-\nabla^2 \phi(r,\underset{\sim}{R})\right]_o d^3R}{\int \left[\phi_o(\underset{\sim}{R})\right]^2 d^3\underset{\sim}{R}}$$

The relationship of the phase shift to $(k_o|V_{el}||k_o)$ in (2.4) is standard,[14] and (2.6) follows from (2.5) if (1.14) and the values of $j_\ell(kr)$ at $r = 0$ are used. The subscript zero on $\phi_o(\underset{\sim}{R})$ and the bracket in the numerator of (2.6) indicates that $r = 0$. We regard (2.4) as the definition of $k_o$ and (2.6) as its evaluation. We use Wang's values of $\kappa$ and $b$; this value of $b$ is close to the experimental one.[7]

Substituting (1.4) into (2.6), we get the value of $k_o^2$

$$(2.7) \qquad k_o^2 = 2\kappa^2 \, \frac{1 + 2\kappa b - \frac{1}{6} (2\kappa b)^2}{1 + 2\kappa b + \frac{1}{3} (2\kappa b)^2}$$

We assume values of $\lambda$ and compute values of $\mu$ satisfying (2.4) and (2.7) by the method described in the appendix. Since $(1/\lambda)$ is essentially the range of $V_{el}(r)$, the basic theory requires $(\lambda b)$ somewhat greater than unity and this guides the choice of values of $\lambda$. We denote the Rayleigh-Ritz estimate of the eigenvalue of $H_o$ by $E_o$, and have

$$(2.8) \qquad E_o = E_W - (\phi, V_{el}\phi)/S$$

where $E_W$ is Wang's estimated energy, namely 3.78 ev.[7] The evaluation of $S$ from (1.4) and (1.17) is straightforward. The integral $(\phi, V_{el}\phi)$ may be written as

$$(2.9) \qquad (\phi, V_{el}\phi) = (\phi, \frac{e^{-\lambda r}}{r} \phi) + \mu \frac{\partial}{\partial \lambda}(\phi, \frac{e^{-\lambda r}}{r} \phi)$$

The second integral on the right of (2.9) is thus obtained from the first by differentiation. The first integral may be written as a sum of two terms, which are counterparts of the usual coulomb and exchange integrals of molecular physics, differing

in that $(e^{-\lambda r}/r)$ replaces $(1/r)$. The direct part is easy because $(e^{-\lambda r}/r)$ is the Yukawa kernel. We evaluated the exchange part by means of the Gegenbauer addition theorem, which is known to quantum chemists as the Barnett-Coulson expansion.[15] The usual method of evaluating the exchange part by using elliptic coordinates[16] was not used because the expansion of the Yukawa kernel involves special functions much more complicated then the Legendre functions which occur in the expansion of the Laplace kernel.

Computed values of the second term on the right of (2.8) are shown in the table. The variation with $\lambda$ of this integral, and with it the expectation value of $H_0$ , is somewhat greater than desired. Since the basic model seems good intuitively, we believe the above approximate evaluation of $k_0$ by (2.6) is responsible for the poor results rather than the use of $U\phi$ as an improved trial function. Another reason for believing (2.6) is a poor value for $k_0$ is that (2.7) leads to negative values of $k_0^2$ for large b. There is no reason why the basic model is worse at large nuclear separations than at equilibrium, providing $\kappa$ is replaced by unity. It would be interesting to study $(k'|V_{el}||k)$ in detail and see how well it can be approximated by a linear function of $k^2$ and $k'^2$ for all values of these arguments which make significant contributions to (2.2), and for the relevant domain of parameters $(\lambda, \mu)$.

# ACKNOWLEDGMENT

A variational expression for $\mu$ is derived from the radial equation by a straightforward generalization of methods used previously.[17] The radial equation is

$$(A1) \qquad \frac{d^2u}{dr^2} + (k_o^2 - V_{el})u = 0$$

where $u$ as usual is the radial function multiplied by $(k_o r)$. Since the phase shift must vanish, $u$ must equal $\sin k_o r$ for values of $r$ much larger than the range of $V_{el}(r)$. We define a function $W$ which vanishes at zero and infinity

$$(A2) \qquad W(r) = u(r) - \sin k_o r$$

Direct substitution leads to

$$(A3) \qquad \frac{d^2W}{dr^2} + (k_o^2 - \frac{e^{-\lambda r}}{r})W - \frac{e^{-\lambda r}}{r} \sin k_o r = -\mu \, e^{-\lambda r}(W + \sin k_o r)$$

If $W_t$ is a function of $r$ which vanishes at zero and infinity, is everywhere continuous, and its derivative has only a finite number of finite discontinuities, a stationary functional for $\mu$ is

$$
(A4) \qquad \mu_t = \frac{\int_0^\infty \left| \left(\frac{dW_t^2}{dr}\right) - k_o^2 W_t^2 + \frac{e^{-\lambda r}}{r}(W_t + \sin k_o r)^2 \right| dr}{\int_0^\infty (W_t + \sin k_o r)^2 e^{-\lambda r} dr}
$$

This functional is useful in a variation-iteration estimate of $\mu$. We start with an estimate of $\mu$, which in practice is the Born approximation, and solve (A3) numerically. We start one solution at $r = 0$ and another at very large $r$, and join them continuously at the point $r_o = (1/\lambda)$. We set $W_t$ equal to this function and use (A4) to obtain a new estimate of $\mu$. Then the new value of $\mu$ is used in (A3) and the method is repeated until successive variational estimates of $\mu$ agree to within rounding errors. In practice convergence is very fast and only three or four iterations are required. The variational estimates of $\mu$ are slightly lower than the Born approximation, and the ratio of these two approximations of $\mu$ is usually $0.97 \pm 0.005$. The effect of using Born approximation instead of the variational estimates upon the expectation value of $V_{el}(r)$ is larger. For example, for $\lambda = 1.5$ atomic units, the Born approximation leads to a value of 0.25 e.v. for the expectation value of $V_{el}(r)$, while the variational estimate of $\mu$ leads to 0.31 e.v., as shown in the table.

Table

Reduction in Zero-Order Energies As a Function of

Range-Determining Parameter

| $\lambda$ atomic units | Expectation Value of $V_{el}(r)$ electron-volts |
|---|---|
| 1.0 | 0.54 |
| 1.5 | 0.31 |
| 2.0 | 0.20 |

# REFERENCES

1.  C. Schwartz, Phys. Rev. $\underline{126}$, 1015 (1962).

2.  W. Lakin, J. Chem. Phys. $\underline{43}$, 2954 (1965)

3.  G.F. Chew, Phys. Rev. $\underline{80}$, 196 (1950).

4.  G.F. Chew and G.C. Wick, Phys. Rev. $\underline{85}$, 636 (1952).

5.  J. Ashkin and G.C. Wick, Phys. Rev. $\underline{85}$, 686 (1952).

6.  G.F. Chew and M.L. Goldberger, Phys. Rev. $\underline{87}$, 778 (1952).

7.  M. Kotani, K. Ohno, and K. Kayama, Quantum Mechanics of Structures of Molecules, Chapter 2, page 17.  This is an article in Handbuch der Physik, Vol. 37, pt. 2, Springer-Verlag, Berlin-Heidelberg-Gottingen (1961).

8.  H.M. James and A.S. Coolidge, J. Chem. Phys. $\underline{1}$, 825 (1933).

9.  W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. $\underline{32}$, 219 (1960).

10. R. Jost and A. Pais, Phys, Rev. $\underline{82}$, 840-51 (1951).

11. Reference 3, equation (4).

12. Reference 4, the material discussed in deriving equations (18) through (22').

13. A. Messiah, Quantum Mechanics, translated by G.M. Femmer, Chapter 10, sec. 20, page 406, North-Holland Publishing Company, Amsterdam (1961).

14. Reference 13, Chapter 10, sec. 17, page 404.

15. F.J. Corbato and A.C. Switendick, Integrals for Diatomic Molecular Calculations.  Article in Methods of Computational Physics, Vol. 2, edited by B. Alder, S. Bernbach, and M. Rotenberg, Academic Press, New York (1963).

16. A. Sommerfeld, <u>Wellenmechanik</u>, Chapter 9, sec. 3, page 636, Friedrich Ungar Publishing Co., New York.

17. P. Morse and H. Feshbach, <u>Methods of Theoretical Physics</u>, Vol. 2, Chapter 9, page 1164, McGraw-Hill Book Co., New York (1953).

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